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ECBC-TR-686

VAPOR PRESSURE OF GB

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April 2009

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20090605265

ABERDEEN PROVING GROUND, MD 21010-5424

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REPORT DOCUMENTATION PAGE

Form Approved OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* XX-04-2009	**2. REPORT TYPE** Final	**3. DATES COVERED** *(From - To)* Apr 2007 - Jun 2007

4. TITLE AND SUBTITLE Vapor Pressure of GB	**5a. CONTRACT NUMBER** **5b. GRANT NUMBER** **5c. PROGRAM ELEMENT NUMBER**
6. AUTHOR(S) Buchanan, James H.; Sumpter, Kenneth B.; Abercrombie, Patrice L.; and Tevault, David E.	**5d. PROJECT NUMBER** 20602384BP0 **5e. TASK NUMBER** **5f. WORK UNIT NUMBER**
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) DIR, ECBC, ATTN: AMSRD-ECB-RT-PF, APG, MD 21010-5424	**8. PERFORMING ORGANIZATION REPORT NUMBER** ECBC-TR-686
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Joint Science and Technology Office of the Defense Threat Reduction Agency, 8725 John J. Kingman Road, Stop 6201, Fort Belvoir, VA 22060-6201	**10. SPONSOR/MONITOR'S ACRONYM(S)** JSTO (DTRA) **11. SPONSOR/MONITOR'S REPORT NUMBER**

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The vapor pressure of isopropyl methylphosphonofluoridate (GB) has been measured using a modified ASTM saturation method between -30 and 20 °C. Those data are combined with experimental data from the literature, and an Antoine fit of the combined data set is presented and compared to the existing fit. The new correlation gives a calculated value for the vapor pressure of GB at 25 °C that is 9.5% higher than the calculated value obtained using the existing correlation.

15. SUBJECT TERMS

GB	Vapor pressure	Gas chromatography	Isopropyl methylphosphonofluoridate
Sarin	Gas saturation	Antoine equation	2-propyl methylphosphonofluoridate
EA 1208	Volatility	107-44-8	2-(fluoro-methyl-phosphoryl)oxypropane

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
U	U	U	UL	22	Sandra J. Johnson **19b. TELEPHONE NUMBER** *(include area code)* (410) 436-2914

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

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PREFACE

The work described in this report was authorized under Project No. 20602384BP0. This work was started in April 2007 and completed in June 2007.

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Acknowledgments

The authors wish to thank Ann Butrow for her helpful vapor pressure discussions and Edward Weller and Leonard Buettner for their testing support.

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VAPOR PRESSURE OF GB

1. INTRODUCTION

Vapor pressure measurements are among the most important physical properties for chemical warfare agents (CWA) because they are used in calculations that determine or influence many other physical properties. Vapor pressure data for CWA are useful in predicting downwind concentration dynamics following dissemination, as well as design of systems to generate and precisely control concentrations of the vapors for toxicology investigations and detector calibration.

In recent work from this Laboratory, we had reported the vapor pressure of persistent nerve agents, VX[1] and Russian VX[2], using a vapor saturation method and analyzed those data in the light of historical data. The measured vapor pressure of these compounds ranged from 8.6×10^{-4} Pa to 3.9×10^{-2} Pa within the experimental temperature range of -13 to +20 °C. Saturated vapor streams were concentrated on solid adsorbents, thermally desorbed, and quantitatively characterized by gas chromatography (GC) using a flame photometric detector, phosphorus mode (FPD-P).

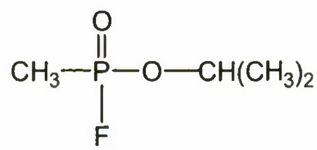
More recently, the U.S. Army Edgewood Chemical Biological Center (ECBC) had reported the vapor pressure of intermediate volatility nerve agents GF[3] and GD[4] and the blister agent HD[5] using the same vapor saturation method and analyzed that data in the light of historical data. The measured vapor pressure of these compounds ranged from 2.8×10^{-2} Pa to 3.0×10^{2} Pa within the experimental temperature range of -25 to +50 °C. Saturated vapor streams for HD were concentrated on solid adsorbents, thermally desorbed, and quantitatively characterized by GC using a flame ionization detector (FID). Saturated vapor streams of GF were sampled using a calibrated GC gas sample loop and quantitatively characterized by GC using an FID. Saturated vapor streams for GD in the -20 to +10 °C temperature range were concentrated on solid adsorbents, thermally desorbed, and quantitatively characterized by GC using an FID. Saturated vapor streams for GD in the +15 to +50 °C temperature range were sampled using a calibrated GC gas sample loop and quantitatively characterized by GC using an FID.

Sarin (GB) is a volatile nerve agent with a previously reported vapor pressure[6] almost one order of magnitude greater than GD at 25 °C and about four orders of magnitude greater than VX at 25 °C. The objective of the present effort is to obtain high-quality vapor pressure data for GB in the ambient to sub-ambient temperature range, between -40 and +25 °C, combine the new data with existing data, and analyze the combined data set.

Sampling the saturated GB vapor using a calibrated GC gas sample loop was not an option for the upper portion of the temperature range for this vapor pressure experiment. Tevault and coworkers successfully combined the saturated vapor stream

method with a gravimetric determination of mass loss using a high purity sample of dimethyl methylphosphonate.[7] This technique was used for the measurement of GB vapor pressure for the upper portion of the temperature range. Saturated vapor streams for GB in the lower temperature range were concentrated on solid adsorbents, thermally desorbed, and quantitatively characterized by GC using an FID.

The vapor pressure of GB has been well-documented in international literature.[6,8-11] The existing measured data was reviewed and evaluated for consistency, combined with the new vapor pressure data described herein, analyzed, fitted, and compared to the existing correlation. The molecular structure of GB is shown below:



Sarin is a volatile, highly toxic nerve agent that has been referred to by many different names: GB; sarin; EA 1208; MFI; IMPF; isopropyl methylphosphonofluoridate; 2-propyl methylphosphonofluoridate; isopropoxymethylphosphoryl fluoride; isopropyl methylfluorophosphonate; methyl fluorophosphoric acid, isopropyl ester; fluorisopropoxymethylphosphine oxide; and O-isopropyl methylfluorophosphonate. The Chemical Abstracts Service (CAS) registry number for GB is 107-44-8 and 50642-23-4.

2. LITERATURE DATA

Harris[8] was the first to report measured vapor pressure data for GB. He used a vapor transference apparatus (vapor saturation) and measured data between 30 and 50 °C. Harris also presented a table of calculated data, from 20 to 50 °C, that was mistakenly identified in Penski's review[6] as isoteniscope measured data and incorrectly included in Penski's calculations to determine GB constants for the Antoine equation. We have included Harris' five experimental data points in the Antoine correlation presented below.

Neale[9] used a validated effusion method to measure the vapor pressure of GB between 5.5 and 19.5 °C and between 0.7 to 2.2 Torr. These data were included in Wardrop and Bryant's report.[10] Neale's five experimental data points are included the Antoine correlation presented below.

Wardrop and Bryant[10] used an isoteniscope to measure the vapor pressure of GB from 45 to 80 °C. They presented eight data points along with Neale's five data points and Harris' five data points in a graphical format with least squares fits for each individual data set. These data are also included in our new Antoine correlation.

Podoll and Parish[11] reported low temperature (-35 to 0 °C) GB vapor pressure data obtained using a dynamic gas saturation method. The 0 and -10 °C measured data were considered outliers because they are not internally consistent with the body of data from the others listed here and, thus, were not included in our calculations to determine GB constants for the Antoine equation. The Podoll and Parish low temperature measured vapor pressure data (-35 and -25 °C) were included in our analysis.

Penski summarized the existing literature data for GB in his 1994 data review and analysis.[6] He did not include the 0 °C Podoll and Parish measured vapor pressure data point (35.9 Pa) in his analysis because the error associated with this point was "2 to 10 times greater than the other values". He did not include the -10 °C Podoll and Parish measured vapor pressure data point (16.8 Pa) in his analysis "due to the fact that it was found to be an outlier". Penski did not include Neale's highest data point (19.5 °C, 291 Pa) in his calculations because the stated upper limit of the method was 133 Pa. Penski mistakenly identified seven Harris[8] calculated data points as isoteniscope measured data and incorrectly included those seven points in his analysis. This error resulted in an artificially high emphasis of the Harris data, which caused an artificially low value for the calculated vapor pressure of GB at 25 °C. The existing GB vapor pressure data from the literature is shown in Table 1.

3. EXPERIMENTAL METHODS

The GB, Chemical Agent Standard Analytical Reference Material (CASARM) lot number GB-U-6184-CTF-N, 10 mL vial number 237, was clear and colorless. It was used as received, other than purging with dry carrier gas as described below.

The glass saturator used in this effort was custom designed at ECBC and has been described previously.[1]

The equipment and procedures used to generate the saturated vapor steam are identical to those used previously[1-5] to measure vapor pressure data in our laboratory and will be briefly described here. Vapor streams saturated with GB were generated by flowing dry nitrogen carrier gas at 25 standard cubic centimeters per minute (sccm) through a glass vessel (i.e., saturator, containing liquid GB of high purity). In this work, the saturator was loaded with 5 g of liquid GB, which was analyzed by gas chromatography-mass spectrometry (GC/MS) before and after vapor pressure data were measured. Both analyses indicated greater than 99 area percent purity with no change in composition after 2 weeks of vapor pressure measurements.

Table 1. GB Literature Vapor Pressure Data (shaded values not used in this analysis).

Temp °C	Temp K	Pressure (Measured) Torr	Pa	Source	Year
30.0	303.15	3.23	430.6	Harris	1945
35.0	308.15	4.21	561.3	Harris	1945
40.0	313.15	5.55	739.9	Harris	1945
45.0	318.15	7.92	1055.9	Harris	1945
50.0	323.15	10.70	1426.5	Harris	1945
5.5	278.65	0.74	98.7	Neale	1948
11.3	284.45	1.13	150.7	Neale	1948
13.1	286.25	1.31	174.7	Neale	1948
16.3	289.45	1.70	226.6	Neale	1948
19.5	292.65	2.18	290.6	Neale	1948
45.0	318.15	9.4	1253.2	Wardrop and Bryant	1952
50.0	323.15	12.2	1626.5	Wardrop and Bryant	1952
55.0	328.15	16.2	2159.8	Wardrop and Bryant	1952
60.0	333.15	20.6	2746.4	Wardrop and Bryant	1952
65.0	338.15	26.4	3519.7	Wardrop and Bryant	1952
70.0	343.15	33.5	4466.3	Wardrop and Bryant	1952
75.0	348.15	42.9	5719.5	Wardrop and Bryant	1952
80.0	353.15	53.2	7092.8	Wardrop and Bryant	1952
0.0	273.15	0.269	35.9	Podoll and Parish	1988
-10.0	263.15	0.126	16.8	Podoll and Parish	1988
-25.0	248.15	0.0440	5.87	Podoll and Parish	1988
-35.0	238.15	0.0163	2.17	Podoll and Parish	1988

The temperature of the saturator was controlled by immersing it in a water-ethylene glycol bath. The temperature of the bath was measured to within 0.1 °C using a calibrated thermometer. Ambient pressure was measured periodically during each run using a Princo Instruments Nova Model mercury barometer (Princo Instruments Inc., Southampton, PA). All barometer readings were corrected for temperature and latitude according to the manufacturer's directions. These readings were used in the vapor pressure calculation as described previously.[1] No corrections were included for pressure drop between the sampling location and ambient. This correction is expected to be minimal because there were no flow restrictions.

Two methods were used in this study to obtain experimental saturator vapor pressure data. The first, used to obtain GB vapor pressure data at 10 °C and 20 °C, was a mass-loss method used by Tevault and coworkers to measure the vapor pressure of dimethyl methylphosphonate.[7] Identical procedures and nearly identical materials were used in this instance to generate the GB saturated vapor stream and to measure mass loss. A smaller version of the saturator cell (Glassblowers.com, Inc., Turnersville, NJ) and a calibrated Mettler (Columbus, OH) Model AM100 laboratory balance, capable of measuring to an accuracy of 0.1 mg, were used. A weight loss of 100 mg was defined as the minimum acceptable value. Calculation of vapor pressure from mass loss was performed as before and assumed the validity of the ideal gas law for GB under these conditions.

The second method was a modification of the ASTM method[12] and was used to obtain GB vapor pressure data between -30 °C and 0 °C. It has been documented in detail in previous reports[1-5] and involves generation of a saturated GB vapor stream at a controlled temperature using the previously described saturator cell, collection and concentration of a calculated volume of GB over a measured time and known flow rate, and determination of the mass of GB collected by GC-FID.

The saturator effluent was sampled as shown in Figure 1 by drawing 5 or 10 standard cubic centimeters per minute (sccm) to a modified ACEM Model 900 (Dynatherm Analytical Instruments Inc., Kelton, PA) adsorbent (tenax) concentrator collection tube maintained at 40 °C for between one and 5 min. The total volume of GB vapor sampled ranged from 5 to 50 standard cubic centimeters. After sample collection, the tenax collection tube was rapidly heated to 275 °C under a flow rate of 20 sccm UHP-grade helium for 5 min and transferred to the ACEM 900 tenax focusing trap maintained at 40 °C. Transfer continued for one additional minute to allow the 10 mm o.d. tenax collection tube to cool. Then, the focusing trap was rapidly heated to 300 °C under a flow rate of 8.0 sccm UHP grade helium for 5 min to affect sample transfer to the gas chromatographic column. The 15 m x 0.53 mm i.d. fused silica GC column (Restek Corp., Bellefonte, PA), with a 1.0 μm RT_x-1 (polydimethylsiloxane) stationary phase, was maintained at 40 °C for 2 min following sample introduction, then heated at a rate of 10 °C/min to 140 °C for a GC run time of 12 min per sample.

A Hewlett-Packard Model 5890 Series II GC equipped with an FID was used as the detection system for the saturator-chromatographic work. Nitrogen was used as the GC carrier gas at a flow rate of 8.0 cc/min and as detector make-up gas at a flow rate of 22.0 cc/min. Combustion gases were air at 400 cc/min and hydrogen at 30 cc/min.

Using the instrumentation and operating conditions described, GB eluted at 5.2 min, which corresponds to a GC column temperature of 72 °C. Saturator GC vapor analyses revealed an extremely high purity sample as the only integrated GC peak corresponded to GB. A small peak eluted at approximately 8 min; however, it was so insignificant in area that it fell below the integration threshold. This trace level peak did not change nor did any new peaks develop indicating no change in sample composition during GB vapor pressure data measurement.

Calibration of the ACEM 900, HP 5890 FID system was accomplished by preparing two calibration standard solutions. Both solutions were prepared by adding an accurately measured amount of GB analyte to the appropriate solvent and correlating the resulting GC integrated peak areas to analyte mass. Thirty microliters of neat CASARM GB (98 mol% pure, sampled from the saturator) was added to about 8 mL of hexane (HPLC Grade, Burdick & Jackson, Muskegon, MI) using a 25 μL Drummond Model 525 Digital Microdispenser and a 5 μL Drummond Model 105 Digital Microdispenser (Drummond Scientific Co., Broomall, PA), then diluting to 10.0 mL with hexane. Converting this volume of GB to mass using the liquid density at room temperature (1.08641 mg/μL at 26.94 °C) and correcting for GB purity (98%) resulted in a solution with a concentration of 3.194 μg GB/μL hexane. The second standard

solution was prepared by adding 10 μL of neat CASARM GB from the saturator to about 8 mL of dichloromethane (Fisher Chemicals, Fair Lawn, NJ) using two additions from the 5 μL Drummond Model 105 Digital Microdispenser and then diluting to 10.0 mL with dichloromethane. Converting this volume of GB to mass using the liquid density at room temperature (1.09067 mg/μL at 23.33 °C) and correcting for GB purity (98%) resulted in a solution with a concentration of 1.06886 μg GB/μL dichloromethane.

The FID response to GB was calibrated as before for HD[5] except where noted. All calibrations were performed during the same day that the standard was prepared. The ACEM 900–5890 FID system was calibrated by making 3 to 5 μL injections of the GB-solvent standard into the distal end of the heated (100 °C) 1/16-in. o.d., 0.040 in. i.d. Sulfinert® tubing, which was supplied with dry nitrogen carrier gas at a flow rate of 10 sccm. ACEM 900 and GC operating parameters were identical to those used for experimental data acquisition with one exception. The ACEM 900 external sampling time for calibration data was always maintained at 15 min to allow sufficient time for GB transfer to the tenax sampling tube. The resulting calibration curve is shown in Figure 2 and was generated by plotting FID area counts versus mass of GB injected for the combined high standard and low standard calibration runs, duplicate injections at each volume. Equation 1 (below) describes the calibration data set most accurately given the constraint that the calibration curve goes through the origin.

$$y = mx \qquad (1)$$

where

y	=	GC-FID area (10^6 area counts)
x	=	analyte mass injected (μg)
m	=	1.7981

Calculation of vapor pressure from the indicated GB mass associated with the measured FID area at each vapor pressure experimental temperature was performed as before.[1]

Calculation of vapor pressure from the indicated GB mass associated with the measured GB weight loss at each vapor pressure experimental temperature was performed as before.[7]

Vapor pressure values are inferred from the measured data using eq 2 (below), as described elsewhere[1] and using the sample purity to correct the indicated vapor pressure by dividing by the GB mole fraction (0.98) in accord with Raoult's Law.

$$VP_{GB} = P_{ambient} \cdot n_{GB}/(n_{GB} + n_{carrier}) \qquad (2)$$

where

VP_{GB} = vapor pressure of GB calculated from measured data
$P_{ambient}$ = ambient atmospheric pressure
n_{GB} = number of moles of GB, measured by GC-FID
$n_{carrier}$ = number of moles of nitrogen carrier

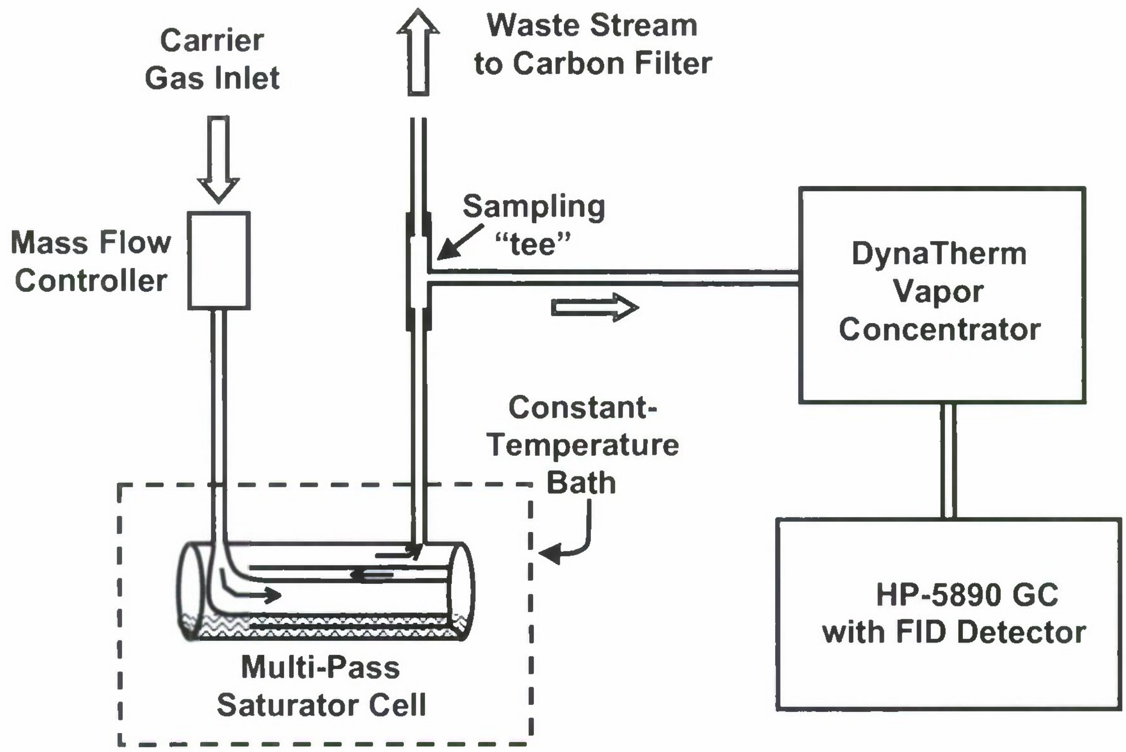


Figure 1. Schematic of Data Acquisition System Used to Measure Low Temperature GB Vapor Pressure Data

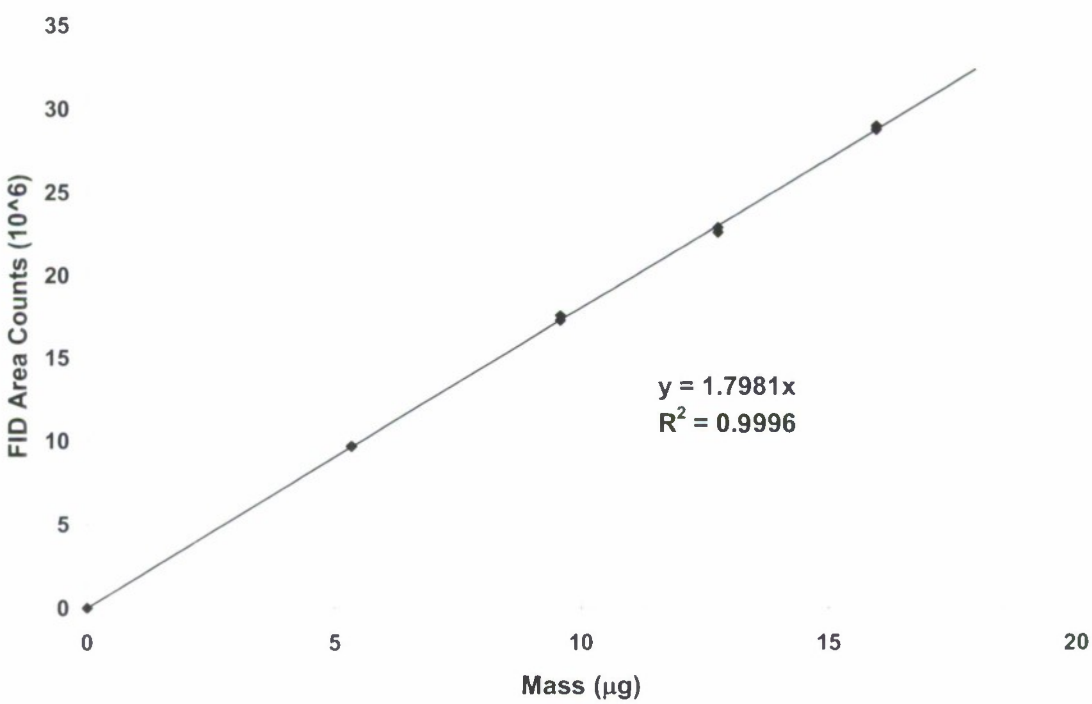


Figure 2. GB Calibration Curve and Analytical Equation

4. RESULTS

Data measured in this work for GB are listed in Table 2 and plotted in Figure 3 along with the GB literature data.[8-11] Penski's fit and the new correlation resulting from combining the new vapor pressure data from this effort with the existing data from the literature are also shown in Figure 3. Figure 4 shows the present data and compares both correlations in the temperature and pressure range of the new data set. Table 3 compares all referenced, measured GB vapor pressure data and the new data set to the new correlation. Table 4 shows the GB data used to generate both fits. Table 5 shows the new Antoine coefficients. Table 6 shows the calculated vapor pressure, volatility, and heats of vaporization for GB based on the new Antoine correlation for GB.

Table 2 shows the measured GB vapor pressure data resulting from six separate saturator determinations at temperatures between -30 to 20 °C. Each of the four Saturator-Chromatographic determined measurements (-30 to 0 °C) is actually the average of between 5 and 15 separate measurements taken after the data acquisition system had stabilized at each new condition. One experiment was performed at a saturator flow rate of 50 sccm. The measured vapor pressure of GB did not change with saturator flow rate, confirming that equilibrium had been achieved at both flow rates. The two Saturator-Gravimetric determined vapor pressure measurements (10 and 20 °C) listed in Table 2 were measured using a saturator flow rate of 10.02 and 10.01 sccm, respectively.

Table 2. GB Vapor Pressure Data Measured in this Work

Temperature		Pressure (Measured)		Method
°C	K	Torr	Pa	
20.0	293.15	1.925	256.62	Saturator-Gravimetric
10.0	283.15	0.952	126.88	Saturator-Gravimetric
0.0	273.15	0.425	56.67	Saturator-Chromatographic
-10.0	263.15	0.187	24.88	Saturator-Chromatographic
-20.0	253.15	0.077	10.27	Saturator-Chromatographic
-30.0	243.15	0.029	3.90	Saturator-Chromatographic

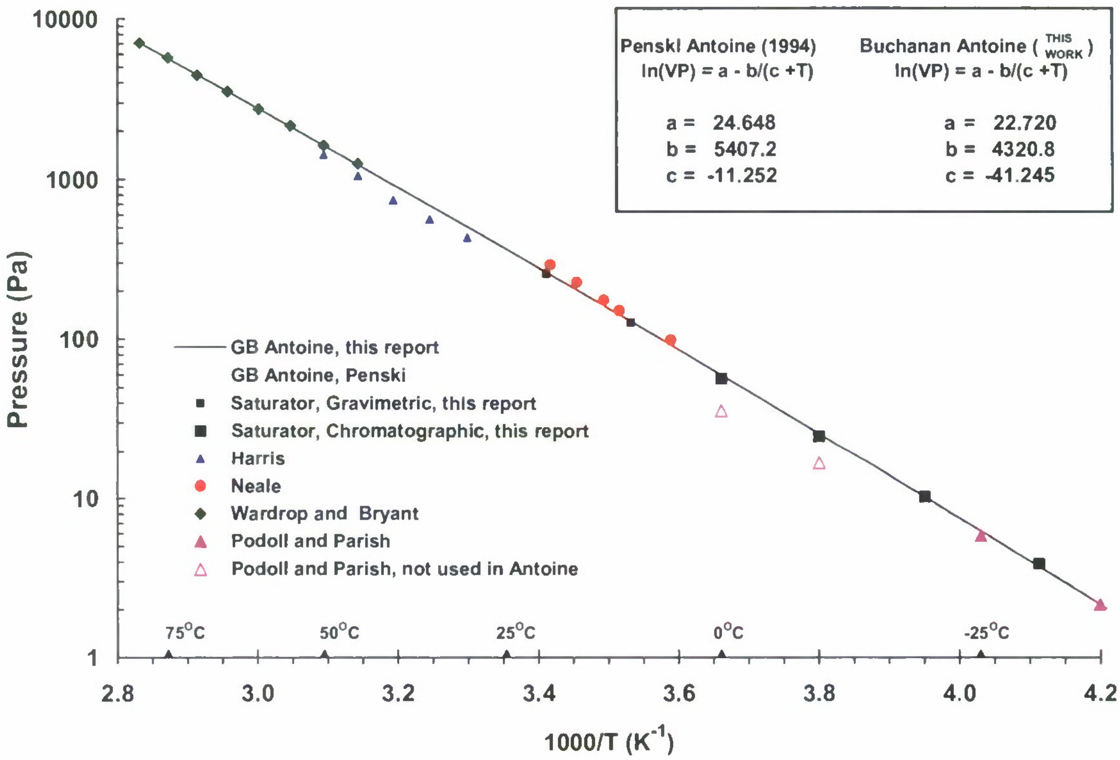


Figure 3. GB Vapor Pressure

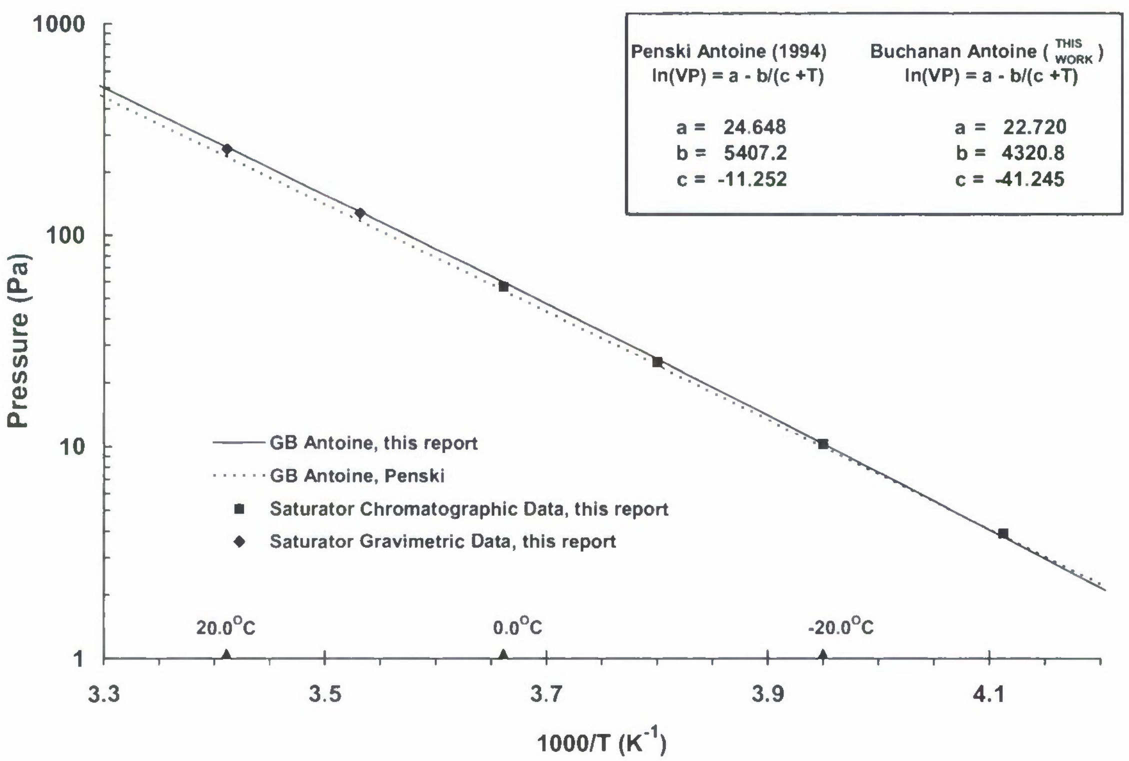


Figure 4. GB Vapor Pressure Comparison

Table 3. Measured GB Vapor Pressure Data Used in Calculations to Generate the New Antoine Correlation for GB (Table 5)

Temperature		Pressure (Pa)		Percent * Difference	Source
°C	K	Calculated	Measured		
-35.0	238.15	2.173E+00	2.173E+00	0.0	Podoll and Parish 1988
-30.0	243.15	3.742E+00	3.898E+00	+ 4.2	This report
-25.0	248.15	6.276E+00	5.866E+00	- 6.5	Podoll and Parish 1988
-20.0	253.15	1.027E+01	1.027E+01	0.0	This report
-10.0	263.15	2.575E+01	2.488E+01	- 3.4	This report
0.0	273.15	5.962E+01	5.667E+01	- 4.9	This report
5.5	278.65	9.180E+01	9.866E+01	+ 7.5	Neale 1948
10.0	283.15	1.288E+02	1.269E+02	- 1.5	This report
11.3	284.45	1.417E+02	1.507E+02	+ 6.3	Neale 1948
13.1	286.25	1.615E+02	1.747E+02	+ 8.2	Neale 1948
16.3	289.45	2.027E+02	2.266E+02	+ 11.8	Neale 1948
19.5	292.65	2.529E+02	2.906E+02	+ 14.9	Neale 1948
20.0	293.15	2.617E+02	2.566E+02	- 1.9	This report
30.0	303.15	5.038E+02	4.306E+02	- 14.5	Harris 1945
35.0	308.15	6.862E+02	5.613E+02	- 18.2	Harris 1945
40.0	313.15	9.242E+02	7.399E+02	- 19.9	Harris 1945
45.0	318.15	1.231E+03	1.056E+03	- 14.3	Harris 1945
45.0	318.15	1.231E+03	1.253E+03	+ 1.8	Wardrop and Bryant 1952
50.0	323.15	1.624E+03	1.427E+03	- 12.2	Harris 1945
50.0	323.15	1.624E+03	1.627E+03	+ 0.2	Wardrop and Bryant 1952
55.0	328.15	2.121E+03	2.160E+03	+ 1.8	Wardrop and Bryant 1952
60.0	333.15	2.745E+03	2.746E+03	0.0	Wardrop and Bryant 1952
65.0	338.15	3.523E+03	3.520E+03	- 0.1	Wardrop and Bryant 1952
70.0	343.15	4.483E+03	4.466E+03	- 0.4	Wardrop and Bryant 1952
75.0	348.15	5.660E+03	5.720E+03	+ 1.1	Wardrop and Bryant 1952
80.0	353.15	7.093E+03	7.093E+03	0.0	Wardrop and Bryant 1952

*Percent Difference = (Measured – Calculated)/Calculated x 100

Table 4. Measured GB Vapor Pressure Data Used to Generate Correlations

Temperature		Measured Pressure		Included in Correlation		Data Source
°C	K	Torr	Pa	PENSKI 1994	THIS WORK	
30.0	303.15	3.23	430.6	YES	YES	Harris 1945
35.0	308.15	4.21	561.3	YES	YES	Harris 1945
40.0	313.15	5.55	739.9	YES	YES	Harris 1945
45.0	318.15	7.92	1055.9	YES	YES	Harris 1945
50.0	323.15	10.70	1426.5	YES	YES	Harris 1945
5.5	278.65	0.74	98.7	YES	YES	Neale 1948
11.3	284.45	1.13	150.7	YES	YES	Neale 1948
13.1	286.25	1.31	174.7	YES	YES	Neale 1948
16.3	289.45	1.70	226.6	YES	YES	Neale 1948
19.5	292.65	2.18	290.6	no	YES	Neale 1948
45.0	318.15	9.4	1253.2	YES	YES	Wardrop and Bryant 1952
50.0	323.15	12.2	1626.5	YES	YES	Wardrop and Bryant 1952
55.0	328.15	16.2	2159.8	YES	YES	Wardrop and Bryant 1952
60.0	333.15	20.6	2746.4	YES	YES	Wardrop and Bryant 1952
65.0	338.15	26.4	3519.7	YES	YES	Wardrop and Bryant 1952
70.0	343.15	33.5	4466.3	YES	YES	Wardrop and Bryant 1952
75.0	348.15	42.9	5719.5	YES	YES	Wardrop and Bryant 1952
80.0	353.15	53.2	7092.8	YES	YES	Wardrop and Bryant 1952
0.0	273.15	0.269	35.9	no	no	Podoll and Parish 1988
-10.0	263.15	0.126	16.8	no	no	Podoll and Parish 1988
-25.0	248.15	0.0440	5.87	YES	YES	Podoll and Parish 1988
-35.0	238.15	0.0163	2.17	YES	YES	Podoll and Parish 1988
20.0	293.15	1.57*	209.3	YES	no	Harris/Penski 1994*
25.0	298.15	2.21*	294.6	YES	no	Harris/Penski 1994*
30.0	303.15	3.08*	410.6	YES	no	Harris/Penski 1994*
35.0	308.15	4.25*	566.6	YES	no	Harris/Penski 1994*
40.0	313.15	5.80*	773.3	YES	no	Harris/Penski 1994*
45.0	318.15	7.84*	1045.2	YES	no	Harris/Penski 1994*
50.0	323.15	10.50*	1399.9	YES	no	Harris/Penski 1994*
56.7	329.85	15.00**	1999.8	YES	no	Harris/Penski 1994**
20.0	293.15	1.925	256.62	no	YES	This report
10.0	283.15	0.952	126.88	no	YES	This report
0.0	273.15	0.425	56.67	no	YES	This report
-10.0	263.15	0.187	24.88	no	YES	This report
-20.0	253.15	0.077	10.27	no	YES	This report
-30.0	243.15	0.029	3.90	no	YES	This report

*Data calculated by Harris and erroneously identified by Penski as measured.[6]

**Reduced pressure boiling point data referenced by Harris; used by Penski in his correlation.[6]

Table 5. New Antoine Correlation for GB Based on Data Published by Harris,[8] Neale,[9] Wardrop and Bryant,[10] and Podoll and Parish[11] Combined with the GB Vapor Pressure Data Measured in this Work (Table 2)

Antoine Parameter	Value
a	22.720
b	4320.8
c	- 41.245
ln(P) = a - b/(c + T)	
P= Pressure (Pascal) and T = Temperature (K)	

Table 6. Calculated* Vapor Pressure, Volatility and Heats of Vaporization for GB Based on the New Antoine Correlation for GB (Table 5)

Temperature		**Vapor Pressure**		**Volatility**	**Heat of Vaporization**	
°C	**K**	**Pascal**	**Torr**	**mg/m^3**	**kcal/mol**	**kJ/mol**
-40	233.15	1.227E+00	9.204E-03	8.868E+01	1.267E+01	5.302E+01
-35	238.15	2.174E+00	1.630E-02	1.538E+02	1.256E+01	5.255E+01
-30	243.15	3.743E+00	2.807E-02	2.594E+02	1.245E+01	5.210E+01
-25	248.15	6.278E+00	4.709E-02	4.262E+02	1.235E+01	5.167E+01
-20	253.15	1.028E+01	7.707E-02	6.839E+02	1.225E+01	5.127E+01
-15	258.15	1.644E+01	1.233E-01	1.073E+03	1.216E+01	5.088E+01
-10	263.15	2.575E+01	1.932E-01	1.649E+03	1.207E+01	5.052E+01
-5	268.15	3.955E+01	2.967E-01	2.485E+03	1.199E+01	5.017E+01
0	273.15	5.963E+01	4.473E-01	3.678E+03	1.191E+01	4.984E+01
5	278.15	8.836E+01	6.628E-01	5.353E+03	1.184E+01	4.952E+01
10	283.15	1.288E+02	9.663E-01	7.666E+03	1.176E+01	4.922E+01
15	288.15	1.850E+02	1.387E+00	1.082E+04	1.169E+01	4.893E+01
20	293.15	2.618E+02	1.964E+00	1.505E+04	1.163E+01	4.865E+01
25	298.15	3.655E+02	2.742E+00	2.066E+04	1.156E+01	4.838E+01
30	303.15	5.039E+02	3.780E+00	2.801E+04	1.150E+01	4.813E+01
35	308.15	6.864E+02	5.148E+00	3.753E+04	1.144E+01	4.788E+01
40	313.15	9.244E+02	6.934E+00	4.974E+04	1.139E+01	4.765E+01
45	318.15	1.232E+03	9.238E+00	6.523E+04	1.133E+01	4.742E+01
50	323.15	1.624E+03	1.218E+01	8.469E+04	1.128E+01	4.720E+01
60	333.15	2.746E+03	2.060E+01	1.389E+05	1.118E+01	4.679E+01
70	343.15	4.484E+03	3.363E+01	2.202E+05	1.109E+01	4.641E+01
80	353.15	7.094E+03	5.321E+01	3.385E+05	1.101E+01	4.605E+01
90	363.15	1.091E+04	8.183E+01	5.062E+05	1.093E+01	4.572E+01
100	373.15	1.635E+04	1.226E+02	7.381E+05	1.085E+01	4.541E+01
110	383.15	2.392E+04	1.794E+02	1.052E+06	1.078E+01	4.511E+01
120	393.15	3.426E+04	2.570E+02	1.468E+06	1.072E+01	4.484E+01
130	403.15	4.810E+04	3.608E+02	2.010E+06	1.065E+01	4.458E+01
140	413.15	6.630E+04	4.973E+02	2.704E+06	1.060E+01	4.433E+01
150	423.15	8.988E+04	6.741E+02	3.579E+06	1.054E+01	4.410E+01
154.1	427.24	1.013E+05	7.600E+02	3.996E+06	1.052E+01	4.401E+01

*Caution should be exercised when using calculated vapor pressure, volatility and heats of vaporization values that are outside of the experimental GB data range (-35 to 80 °C).

5. DISCUSSION

The agreement between the data measured in this work and those reported previously by Harris,[8] Neale,[9] Wardrop and Bryant,[10] and Podoll and Parish[11] is very good. The average error of the measured GB vapor pressure data (Table 3) used in calculations to generate the new Antoine correlation for GB (Table 5) is about 6%. It should be noted that the vast majority of residual error is attributable to the early vapor transference[8] and effusion[9] data, and if the current data is correlated with the isoteniscope[10] data and more recent saturator[11] data of Podoll and Parish only, the data sets line up much more precisely, with a residual average error of about 1.5%, and that correlation equation is only slightly different (ca. 1.5% lower) than the one presented here. As is obvious in Figure 3, Neale's data deviate from our Antoine correlation monotonically to higher error as temperature increases, with an average difference of about 10%. Harris' data deviate to the low side of our Antoine equation, with an average difference of about 15%. It is likely that each of those data sets was plagued by unknown systematic errors, fortunately of similar magnitude and opposite direction, and as a result, they tend to offset each other in our analysis.

The new correlation gives a calculated value for the vapor pressure of GB at 25 °C that is 9.5% higher than the value calculated by Penski at the same temperature. The fact that the new correlation is significantly different from the 1994 Penski correlation can be understood upon examination of the data sets used to generate the two fits. Table 4 shows the specific data points used in the calculations to generate Antoine coefficients for the Penski fit (1994) and our new fit. Penski's data set contains 27 data points, and ours contains 26; however, the Penski data set mistakenly included seven data points from Harris that were calculated, not measured. In his report, Penski misidentified those as isoteniscope data, which led to their erroneous inclusion in his calculations that ultimately defined the GB vapor pressure curve.

The average error associated with the five Harris measured data points, relative to the new fit, is -16%. By adding the seven calculated data points to his assessment, Penski essentially double-weighted the Harris data set, which resulted in an artificially low calculated vapor pressure for GB in the ambient temperature region. The origin of the reduced pressure boiling point datum (56.7 °C) is unclear, but consistent with the rest of the Harris data, contributing to the discrepancy between the data sets. The Harris data accounted for 13 of the 27 points (48%) in Penski's analysis, biasing the data inappropriately.

The measured saturator vapor pressure data described in this report has defined the sub-ambient region of the GB vapor pressure curve and has significantly aided in redefining the ambient region. The average error associated with the six saturator measured data points described in this report, relative to the new fit, is about 1%, which is comparable to previous results from our laboratory and is considered to represent excellent precision in the data measurement. Table 6 lists calculated vapor pressures, volatility, and heats of vaporization for GB at selected intervals over the range of -40 to 150 °C based on the present data. Caution should be exercised when

using calculated vapor pressure, volatility and heats of vaporization values that are outside of the experimental GB data range (-35 to 80 °C). The standard boiling point projected for GB based on the present work is 154.1 °C.

6. CONCLUSIONS

Sarin (GB) vapor pressure has been measured using saturator-gravimetric and saturator-gas chromatographic methods. The Antoine analysis has been updated based on the data reported herein and reliable literature vapor pressure data. The vapor pressure of GB at 25 °C is estimated to be 9.5% higher than previously reported, which is near the maximum discrepancy between the new and old correlations. The difference between these correlations decreases until they cross at around -28 and 97 °C. It is our conclusion that the previous correlation[6] inappropriately weighted the Harris data, and that the correlation presented here corrects that error, fills in the data gap in the ambient temperature range, and verifies Penski's earlier assertion that the two highest Podoll and Parish data points were flawed and should not be considered as being reliable. The data presented herein line up extraordinarily well with isoteniscope data measured 57 years earlier. It is our conclusion that the Wardrop and Bryant data and the new data presented in this report are the most reliable data sets measured to date.

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